

# Shubnikov–de Haas effect in graphite intercalation compounds of the first and second orders

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High-quality single crystals of intercalation compounds of graphite with  $\text{AlCl}_3$  of first order and with  $\text{ICl}$  of second order have been synthesized. These crystals exhibit distinct Shubnikov–de Haas oscillations. The extreme cross-sectional areas of the Fermi surface, their angular dependence, and the effective masses and concentrations of the current carriers at liquid-helium temperatures have been determined.

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Intercalation compounds of graphite are attracting considerable interest because of their “supermetallic” electrical conductivity. The conductivity of the compound  $\text{C}_{6.5}\text{SbF}_5$  at room temperature, for example, is several times higher than that of copper or silver.<sup>1</sup> During the formation of such compounds, the atoms of the intercalate penetrate into the regions between the carbon layers, significantly increasing the

distance between these layers,  $C_0$ . While a graphite single crystal has  $C_0 = 3.354 \text{ \AA}$ , for example, the component  $C_{9,3}AlCl_{3,3}$  has  $C_0 = 9.541 \text{ \AA}$ . In intercalation compounds of first order, the intercalate layers alternate with the monatomic graphite layers. In the compounds of second order, the intercalate layers are found after each two monatomic graphite layers.

At present, we have essentially no information on the structure of the energy spectrum of intercalation compounds of graphite or on the mechanisms responsible for their very high conductivity. One effective method for obtaining such information is to study the Shubnikov-de Haas effect. To the best of our knowledge, however, no one has so far been successful in observing Shubnikov-de Haas oscillations in first-order intercalation compounds of graphite. The only oscillations which have been observed are small oscillations of complex structure exhibited by second- and higher-order compounds of graphite with chlorides of certain transition metals ( $FeCl_3$ ,  $CdCl_2$ ,  $PdCl_2$ ) in fields of about 200 kOe (Ref. 2).

In this letter we are reporting the first observation and study of distinct Shubnikov-de Haas oscillations (the oscillation amplitude is comparable to the change in the monotonic component of the resistance in a magnetic field!) in fields up to 60 kOe in the compounds  $C_{9,3}AlCl_{3,3}$  (first order) and  $C_{16}ICl$  (second order).

To synthesize high-quality quasi-single-crystal intercalation compounds we used high-quality pyrolytic graphite annealed at  $> 3000^\circ\text{C}$ . The intercalation order was determined by x-ray structural analysis and chemical analysis. The samples were quasi-single crystals  $5 \times 0.5 \times 0.5 \text{ mm}$  in size. For the measurements, carried out by the four-contact method, contacts of gold wire were cemented to the samples with silver paste. The signal from the "potential" or Hall contacts was fed to an F116/1 "photocompensation" amplifier and recorded on an  $x$ - $y$  chart recorder.

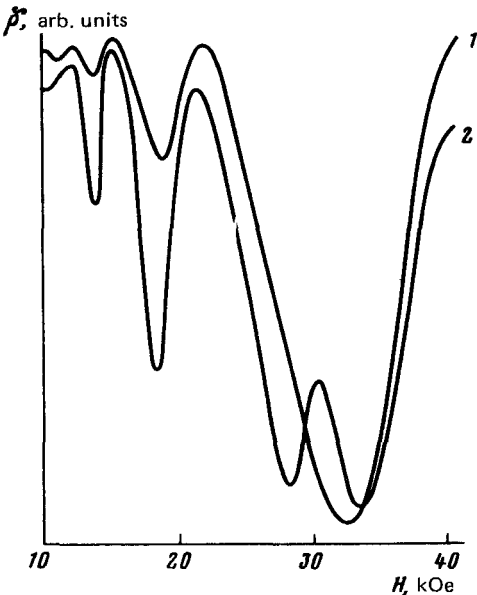


FIG. 1. Dependence of the oscillatory part of the magnetoresistance,  $\rho$ , on the magnetic field  $H$ , along the  $C$  axis, at 4.2 K. 1—Pyrolytic graphite sample annealed at  $\sim 3000^\circ\text{C}$ ; 2—samples annealed at  $> 3000^\circ\text{C}$ .

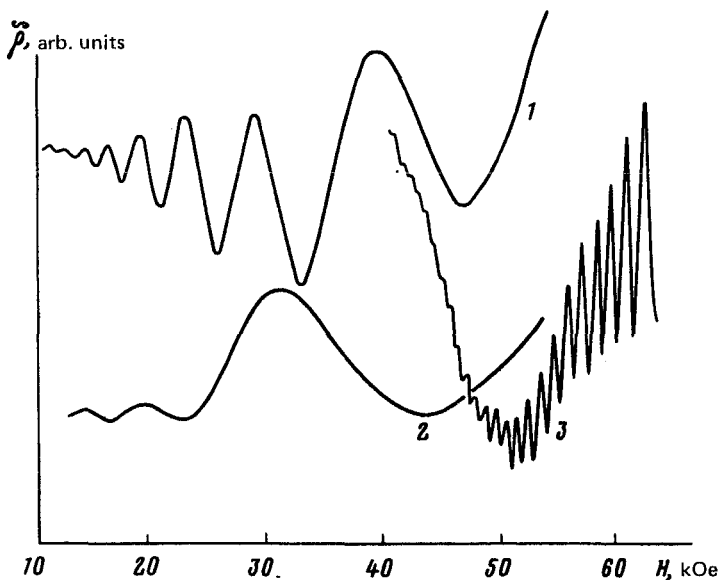


FIG. 2. Dependence of the oscillatory part of the magnetoresistance on the magnetic field  $H$ , along the  $C$  axis, at 4.2 K. 1—For a  $C_{9,3}AlCl_{3,3}$  sample; 2—for the same sample, after a 2-day hold; 3—for a  $C_{16}ICl$  sample.

Figures 1 and 2 illustrate the results with curves of the oscillations of the magnetoresistance of pyrolytic graphites subjected to various types of heat treatment and of intercalation compounds of the first and second orders at liquid-helium temperatures at fields up to 60 kOe. In the case of the compound  $C_{9,3}AlCl_{3,3}$  the oscillations are strictly monochromatic, and their frequency is quite different from the oscillation frequency of the original graphite. As time elapses the oscillation frequency of these  $C_{9,3}AlCl_{3,3}$  samples changes, while the distance between atomic layers remains constant. From the latter circumstance we can determine how the effective mass of the current carriers depends on the extreme cross-sectional area of the Fermi surface, from measurements taken from a single sample. As this area decreases from  $S = (10.62 \pm 0.10) \times 10^{-42} \text{ g}^2 \cdot \text{cm}^2/\text{s}^2$  to  $S = (5.41 \pm 0.10) \times 10^{-42} \text{ g}^2 \cdot \text{cm}^2/\text{s}^2$ , the effective mass falls from  $m^* = (0.057 \pm 0.002)m_0$  to  $m^* = (0.051 \pm 0.002)m_0$ . As the angle ( $\theta$ ) between the basis plane and the magnetic field direction is increased, the extreme areas increase in proportion to  $\cos^{-1}\theta$ . These extreme cross-sectional areas can thus be identified with the hole part of the Fermi surface, which is a smooth cylinder whose axis passes through point  $H$  in the Brillouin zone.<sup>3,4</sup> For the compound  $C_{16}ICl$  (of second order) we also observe Shubnikov-de Haas oscillations; their amplitude is comparable to the magnitude of the monotonic component of the magnetoresistance. The extreme cross-sectional area corresponding to these oscillations is  $S = (312 \pm 3) \times 10^{-42} \text{ g}^2 \cdot \text{cm}^2/\text{s}^2$ , or  $\sim 50$  times larger than that of the original graphite. The Hall coefficient  $R$  of these graphite compounds is positive at liquid-helium temperatures and slightly dependent on the strength of the magnetic field up to 60 kOe. For  $C_{9,3}AlCl_{3,3}$  at 4.2 K we find  $R \approx 0.5 \text{ cm}^3/\text{C}$ .

From these results we can directly determine the concentration of the current carriers (holes) in these intercalation compounds of graphite:  $n_h = 1.02 \times 10^{19} \text{ cm}^{-3}$  for  $\text{C}_{9.3}\text{AlCl}_{3.3}$  and  $n_h = 27.4 \times 10^{19} \text{ cm}^{-3}$  for  $\text{C}_{16}\text{ICl}$ . The values found for  $n_h$  for  $\text{C}_{9.3}\text{AlCl}_{3.3}$  agree well with the estimate  $n_h = 1/R |e|$ , indicating that this compound has only a single group of carriers.

It can thus be concluded from these results that the formation of the intercalation compound is accompanied by a sharp increase in the carrier concentration, apparently because of a redistribution of the electron density between graphite and intercalate layers.

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1. F. L. Vogel, *J. Mater. Sci.* **12**, 982 (1977).
2. J. A. Woollam, E. Haugland, M. B. Dowell, N. Kambe, E. Mendez, F. Hakimi, G. Dresselhaus, and M. S. Dresselhaus, *Carbon* **18**, 55 (1980).
3. T. C. Chieu, G. Dresselhaus, and M. S. Dresselhaus, *Solid State Commun.* **37**, 561 (1981).
4. N. A. W. Holzwarth, *Phys. Rev.* **B21**, 3665 (1980).

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